

Photolysis Products and Absorption Cross Sections of the ClO Dimer

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Abstract

Both the photolysis products and absorption cross sections of the ClO dimer, ClOOC1, are important to the photochemistry of the polar winter. In this work dimer photolysis was studied at the wavelength 254 nm, at 195 K. The dimer was prepared by the photolysis of Cl₂O at 254 nm. As dimer appeared, it absorbed a significant fraction of the 254 nm light. By following the rate of photolysis of Cl₂O, it was possible to distinguish between possible dimer photolysis paths producing either Cl + ClOO or ClO + ClO. The results indicate that the former path predominates, in agreement with earlier literature results. Measurements were also made of the dimer cross sections. The results yield somewhat lower cross sections in the longer wavelength region (>300 nm) than those obtained by previous workers.

Introduction

The ClO dimer is formed by the self-reaction of ClO radicals at the low temperatures of the polar winter. When sunlight is present, the dimer is thought to take part in catalytic ozone destruction by yielding chlorine atoms upon photolysis, followed by attack of the chlorine atoms on ozone.



In addition to the photolysis path yielding Cl and ClOO radicals, another path yielding ClO + ClO is possible.



This path would not contribute to ozone loss, because ClO is inert to ozone. Although it is normally assumed in atmospheric models that only the Cl + ClOO branch is important, the experimental basis for this assumption is somewhat uncertain. Cox and Hayman¹ concluded that

Cl and ClOO are the major dimer photolysis products by modeling the disappearance of Cl₂O and the appearance of dimer in the photolysis of Cl₂O at 254 nm, at temperatures of 203-233 K. However, they placed an uncertainty of approximately a factor of two on the result.

In the most direct study at a wavelength appropriate for atmospheric photolysis of dimer, Molina et al.² reported a quantum yield of approximately unity for the Cl + ClOO path at 308 nm. That result was based on measurements of the Cl-atom LIF signal in the photolysis of the dimer (235 K, 20 Torr) compared to the Cl-atom LIF signal when photolyzing Cl₂ (also at 308 nm). However, the authors used a value of 22 for the ratio of the dimer cross section at 245 nm and 308 nm, as determined in their own work. If one takes that ratio from the NASA recommended dimer cross sections,³ the value is 13 and the corresponding Cl + ClOO quantum yield would be only 0.6. That would imply that the ClO + ClO path makes a 40% contribution. Thus, there is again about a factor of two uncertainty in the photolysis branching ratio, related to the combined uncertainties in the cross sections and the Cl yield.

Jacobs et al.⁴ studied ClOOCl photolysis in argon matrices at cryogenic temperatures (liquid He) and found that ClOCIO was a product. Assuming that ClO must have been the precursor of the ClOCIO, they concluded that the ClO + ClO channel is significant in dimer photolysis. They did not give a quantitative estimate of the branching ratio.

Eberstein⁵ argued that dimer photolysis should proceed by path (4) on the grounds that the O-O bond in ClOOCl is much weaker than the Cl-O bond. However, Eberstein assumed that the Cl-O bond energy in ClOOCl is similar to that of the ClO radical (about 64 kcal/mole). Actually, the Cl-OOCl bond energy is only about 21 kcal/mole, just slightly greater than the ClO-OCI bond (18 kcal/mole)³. Thus, an argument based on preferential breaking of the weaker bond is not compelling in this case.

Previous studies of the dimer spectrum^{1,6,7} have all used Cl₂O as the source of ClOOCl. The absorption cross sections are difficult to measure, because the compound is stable only at low temperatures and cannot be prepared in the pure state. The spectrum has only been obtained in the presence of other molecules such as Cl₂, O₃, or Cl₂O, and the net ClOOCl spectrum must be extracted by deconvolution of the composite spectra. This process is somewhat qualitative in nature and is subject to error. The situation is similar to the case of HOCl, for which previous cross section measurements have been erroneous due to contamination with Cl₂O and Cl₂.⁸ The dimer spectrum may also be contaminated by absorption due to other by-products of the photochemical system, such as Cl₂O₃, which can appear at low temperatures when ClO and OClO are present. The latter compound, OClO, is produced in the ClO + ClO reaction at temperatures above about 230 K. Some of the largest cross section errors occur in the "tail" region above 300 nm, where the spectrum is weak. The errors arise from the necessity to correct the spectrum for

Cl₂ and from baseline errors in the total spectrum. This wavelength region is the most important for determining the atmospheric photolysis rates of ClOOCl.

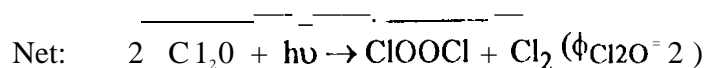
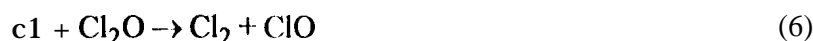
Experimental

Apparatus.

The ClO dimer was prepared as before⁷ by photolysis of Cl₂O mixtures. The Cl₂O was produced by oxidation of Cl₂ over HgO at low temperature.⁹ The experiments were performed in a low-temperature, 5-cm path length spectrophotometric cell of quartz construction. The cell was cooled by a surrounding jacket containing a dry-ice/methanol mixture. Some early experiments were performed in a metal cell of similar construction, with halocarbon coating on the walls. However, dimer was found to be more stable in the quartz cell. The cell was evacuated and filled with Cl₂O at a pressure of about 10 torr, and then pressurized to about three atm with nitrogen to reduce diffusion to the walls. A low pressure mercury lamp was used for irradiation at 254 nm. The UV absorption spectra were taken from 200-400 nm with a Cary Model 4E spectrometer.

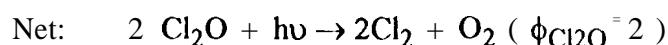
Dimer Photolysis Products.

The concept for distinguishing between reactions (1) and (4) for the dimer photolysis is based on the fact that in the photolysis of Cl₂O/ClOOCl mixtures the quantum yield of Cl₂O loss (calculated for total light absorption by both species) would be constant and independent of the Cl₂O to ClOOCl ratio, provided that ClOOCl photolysis yields only Cl + ClOO. This can be seen from the mechanisms shown below, the first of which accounts for light absorption by Cl₂O and the second for light absorption by ClOOCl:



By this mechanism the quantum yield for Cl₂O photolysis is exactly 2, since at the low temperature of the present experiment the self-reaction of ClO gives only dimer and does not regenerate atomic Cl, as it does at higher temperatures.⁷

As dimer accumulates, it absorbs an increasing fraction of the 254 nm radiation, with two effects: (1) it reduces the amount of light available to Cl₂O, and (2) it increases the total light absorption by the mixture. The net effect on the rate of Cl₂O loss depends on the products of dimer photolysis. If dimer photolysis proceeds by reaction (1), the quantum yield for Cl₂O loss (calculated on the basis of total light absorbed by both species) remains equal to 2:



Note that any reaction of atomic Cl with dimer leads to no net loss of Cl, because Cl is regenerated and only dimer is lost:



Thus, the quantum yield for Cl_2O loss would remain constant if the dimer photolysis proceeds only by reaction (1). To the extent that dimer photolysis produces ClO, the rate would be reduced. The sensitivity to the dimer product ratio is shown in Figure 1, for the test cases where reaction (4) contributes 0%, 30%, and 60% to the dimer photolysis. The data in Figure 1 were obtained by means of a computer simulation using the reaction set shown in Table 1, taking into account the relative absorbance of Cl_2O and ClOOCl. As expected, the rate of Cl_2O photolysis remains exactly constant for the case where reaction (4) does not occur, but declines with increasing ClO production.

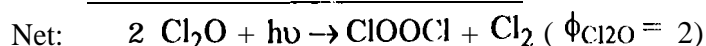
There is one complication in Cl_2O photolysis which must be considered. There is evidence^{10,11} that Cl_2O photolysis at wavelengths near 254 nm proceeds not only by reaction (5), but also gives atomic oxygen by one or both of the following steps:



The thresholds for (9) and (10) are 713 nm and 292 nm, respectively. Unfortunately, the exact contributions of these processes are not known, particularly as a function of wavelength. In the present experiments we have confirmed that atomic oxygen is produced (from the production of O_3 in O_2 -containing mixtures) and have found the yield at 254 nm to be about 50%. This is somewhat

less than the earlier workers¹¹, who suggested yields of about 25%, but over a broader wavelength region.

Of the two possible steps listed above for production of atomic oxygen, reaction (9) would not affect the experiment because $\phi_{\text{Cl}_2\text{O}}$ would remain equal to two:



The expected insensitivity to reaction (9) was confirmed by computer simulations in which up to 30% of the photolysis was allowed to proceed by this path, with no change in the resulting photolysis rate. However, reaction (10) would cause an increase in the rate of Cl_2O loss, because of the increased yield of atomic species. Figure 2 shows the effect of dimer photolysis for the case where 1 So/O of the Cl_2O photolysis gives $\text{Cl} + \text{Cl} + \text{O}$. This is three times what we find experimentally for the total atomic oxygen yield, and is viewed as an upper limit to the contribution of that path. In this case the normalized Cl_2O loss rate is reduced in the presence of dimer, even when the dimer photolysis gives no ClO. Therefore a reduced Cl_2O loss rate, if observed, could be due either to channel (4) for dimer photolysis or channel (10) for Cl_2O photolysis, or both. Considering our experimental evidence that atomic oxygen production is quite small at 254 nm, little effect due to channel (10) would be expected.

Dimer Spectrum.

Since it is difficult to obtain reliable cross sections at longer wavelengths by direct experimental measurement (for reasons discussed above), we have concentrated on obtaining data at shorter wavelengths which are free of residual Cl_2O absorption. Those values can then be used for extrapolation above 310 nm. We have looked only at relative cross sections, since the absolute values near the peak are reasonably well established.³ The basic problem is to determine how much of the Cl_2O spectrum to subtract. The subtraction of Cl_2 is a less important problem, because Cl_2 absorption occurs mainly above 300 nm. Three approaches have been used: (1), From the product spectra for each experiment the individual spectra for each component were subtracted from the total spectrum, using the criterion that the peak in the resultant dimer spectrum should be fixed at 244 nm, as determined in earlier work.⁷ (2), Dimer spectra were obtained by taking advantage of the fact that its rate of decomposition in the cell (by wall reactions) is much faster than that of the other components (Cl_2O and Cl_2), and thus the dimer spectrum on a relative basis can be obtained by taking difference spectra. The dimer spectrum

obtained by the difference method may be slightly contaminated with the Cl_2O spectrum, to the extent that decomposition of that species occurs during the time of the dimer decomposition. However, that dimer spectrum should correspond to an upper limit for Cl_2O content, and thus serve as a useful boundary condition for comparison with spectra obtained by the iterative subtraction method. (3), Difference spectra taken in the course of our earlier work⁷, using Cl_2/O_3 mixtures as the dimer source, were compared with the present spectra. The earlier spectra, although less suitable for the measurement of absolute cross sections because of the much lower dimer concentrations, are nevertheless useful for comparison of the shape of the dimer spectrum obtained from the Cl_2O experiments.

Results

Dimer Photolysis Products.

Figure 3 shows the results of the Cl_2O photolysis rate experiments, as a test for the mechanism of dimer photolysis. Two of the three experiments with dimer present show slightly reduced slopes compared to the slopes with no dimer. The average of all three experiments corresponds to a slope reduction of 8%. Based on the sensitivity to product branching ratios as determined in the computer simulations, this corresponds to a yield of the $\text{Cl} + \text{ClOO}$ branch of about 85%. An uncertainty of 15% must be assigned to this result, arising from the experimental uncertainties in measurement of the slopes with and without dimer present.

Dimer Spectrum.

Figure 4 shows dimer spectra as obtained by methods (1-3) above. All have been normalized to $6.4 \times 10^{-18} \text{ cm}^2$ at 244 nm, this being the JPL 94-26¹² recommendation at that wavelength. The NASA recommendation is included for comparison, as is the single measurement at 308 nm by the Molina group (calculated from their ratio $\sigma^{245}/\sigma^{308} = 22$)². Our data are in good agreement among themselves and with the Molina measurement, but are significantly lower than the JPL 94-26 recommendation in the tail, or fall-off region,

Figure 5 is a plot of the logarithms of the cross sections vs. wavelength. Also shown is a linear fit to the Cl_2O data based on the wavelength range 260-310 nm. Above about 310 nm, the logarithmic extrapolation is considered to be a better estimate of the cross sections than the actual data. The extrapolated data are compared in Figure 6 with the data and with JPL 94-26 recommendation. The latter is based on an extrapolation (above 360) nm of previous data^{1,6,7}. Table 2 lists recommended cross sections based on the present work.

Discussion

Dimer Photolysis Products.

The present experiments indicate that the Cl + ClOO branch in ClOOCl photolysis constitutes $85 \pm 15\%$ of the total (at 254 nm). It may be noted that the Molina result,² when adjusted to the current ratio, $\sigma^{245}/\sigma^{308} = 19$, corresponds to $\phi = 0.89$ for that branch at 308 nm. Although a 100% contribution for Cl + ClOO is within the uncertainty of both experiments, it is perhaps unlikely that a photolysis process having two possible branches of nearly equal energy requirements would proceed exclusively by only one path.

Dimer Spectrum and the Antarctic J- Value.

The present results strongly suggest that previous measurements of the dimer cross sections, on which the recommendations in JPL 94-26 (also 92-20) are based, were improperly corrected for Cl₂O, and are too high in the “tail” region. The current results also agree well with the 308 nm cross section value of the Molina group². The difference, although small, has a significant effect on dimer photolysis rates in the Antarctic atmosphere. Most of the contributions to the photolysis rate occur at wavelengths in the 310 to 370 nm range. (See Figure 7). With the new cross sections the total J-value under Antarctic conditions is about 2/3 the value obtained from the JPL 94-26 values.

Acknowledgements.

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Table I: Reaction set for the simulation of Cl₂O photolysis at 254nm and 195 K.

Reaction	Rate Constant cm ³ /molec·s	Reference
Cl ₂ O +- hv → Cl+ ClO	a	
Cl ₂ O + hv → Cl ₂ + O	a	
Cl ₂ O + hv → 2 Cl + O	a	
ClOOCl + hv → Cl+ ClOO	a	
ClOO → cl + O ₂	b	
ClOOCl+ hv → 2 ClO	a	
ClO + ClO → ClOOCl	b	
cl+ Cl ₂ O → Cl ₂ + ClO	1.0E-10	JPL 92-20
cl+- ClOOCl → Cl ₂ + ClOO	1.0E-10	JPL 92-20
cl + " O ₃ → Clo + O ₂	7.6E-12	JPL 92-20
O + O ₂ → O ₃	4.0E-14	JPL 92-20
o + Cl ₂ O → 2 ClO	1.2E-12	JPL 92-20
O + Cl ₂ → ClO + Cl	3.7 E-15	JPL 92-20
o + ClOOCl → ClO + ClOO	1.0E-12	estimate

a. The relative photolysis rates of Cl₂O and ClOOCl were bas-ed on the respective cross sections at 254 nm. (JPL 92-20 values).

b. The reaction is considered instantaneous; i. e., thin-e is no significant competing reaction.

Table 2. Dimer Cross Sections, σ , cm² x 1020.

λ , nm	σ	λ , nm	σ	— — —	λ , nm	σ
200	374.6	284	119.4		368	1.7
202	342.8	286	107.9		370	1.5
204	312.8	288	97.2		372	1.4
206	285.3	290	88.5		374	1.2
208	260.5	292	79.5		376	1.1
210	238.3	294	71.5		378	1.0
212	219.9	296	63.7		380	0.92
214	205.9	298	56.9		382	0.83
216	196.7	300	51.3		384	0.75
218	193.7	302	46.0		386	0.68
220	198.3	304	41.6		388	0.62
222	211.5	306	37.7		390	0.56
224	233.2	308	34.1		392	0.50
226	264.8	310	30.8		394	0.46
228	304.7	312	27.9		396	0.41
230	352.8	314	25.2		398	0.37
232	406.6	316	22.8		400	0.34
234	461.6	318	20.6		402	0.30
236	515.2	320	18.7		404	0.28
238	563.6	322	16.9		406	0.25
240	602.4	324	15.3		408	0.23
242	628.7	326	13.8		410	0.20
244	640.0	328	12.5		412	0.18
246	637.1	330	11.3		414	0.17
248	619.1	332	10.2		416	0.15
250	588.9	334	9.2		418	0.14
252	549.5	336	8.4		420	0.12
254	505.1	338	7.6		422	0.11
256	458.1	340	6.8		424	0.10
258	413.0	342	6.2		426	0.09
260	370.1	344	5.6		428	0.08
262	332.1	346	5.1		430	0.07
264	299.0	348	4.6		432	0.07
266	269.7	350	4.1		434	0.06
268	245.2	352	3.7		436	0.06
270	223.3	354	3.4		438	0.05
272	204.2	356	3.1		440	0.05
274	187.6	358	2.8		442	0.04
276	170.9	360	2.5		444	0.04
278	157.1	362	2.3		446	0.03
280	143.3	364	2.1		448	0.03
282	131.0	366	1.9		450	0.03

Figure Captions

Figure 1. Simulation of **Cl₂O** photolysis showing the effect of simultaneous photolysis of the product ClOOCl as a function of the Cl + ClOO yield.

Figure 2. Simulation of **Cl₂O** photolysis showing the effect of a 15% contribution of the photolysis branch yielding Cl + Cl + O.

Figure 3. Results for the **Cl₂O** photolysis rate with and without ClOOCl present. The solid lines (normalized to the starting concentrations) represent the slopes as determined in experiments in which the dimer was allowed to decay to a negligible concentration between photolysis periods.

Figure 4. ClOOCl cross sections from this work compared to those of JPL 94-26,

Figure 5. Logarithmic plot of the cross section data.

Figure 6. ClOOCl cross sections at longer wavelengths.

Figure 7. Antarctic J-values for ClOOCl.

Figure 1: Huder and DeMore

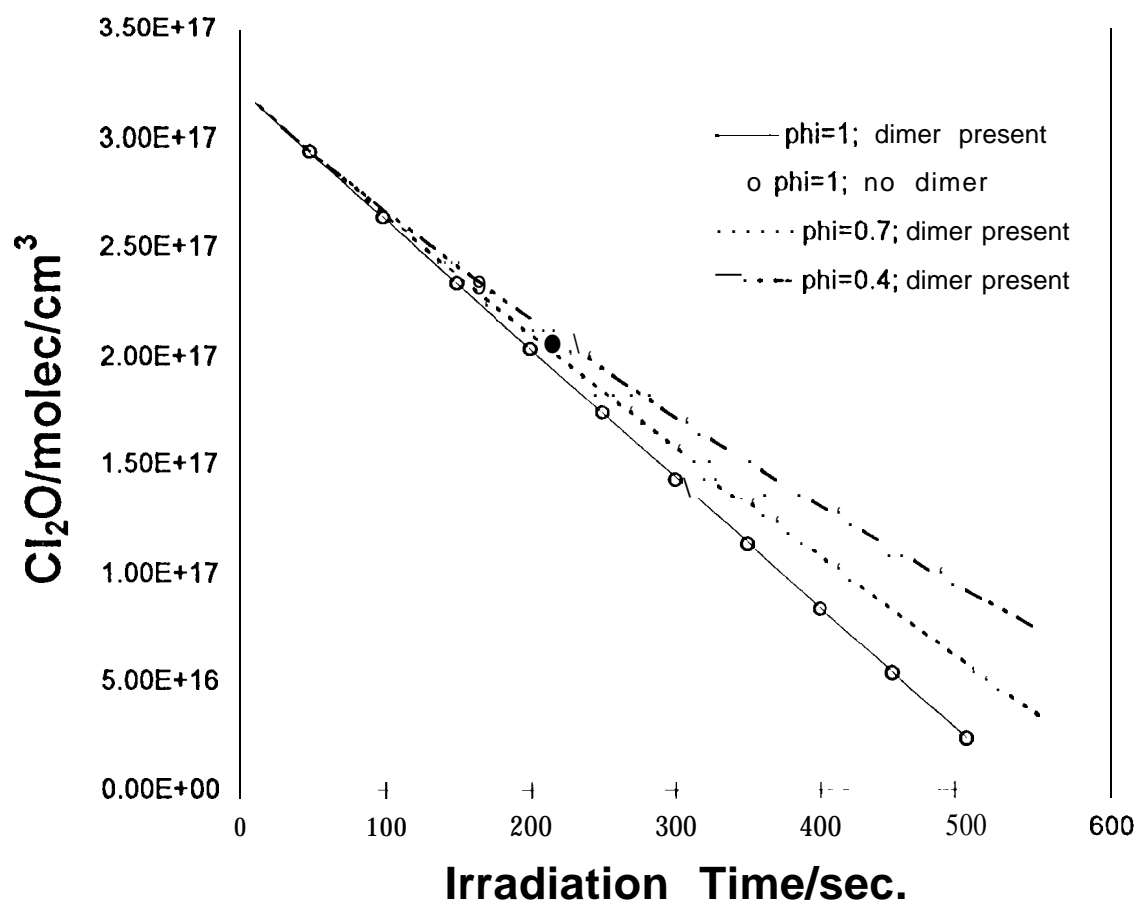


Figure 2: Huder and DeMore

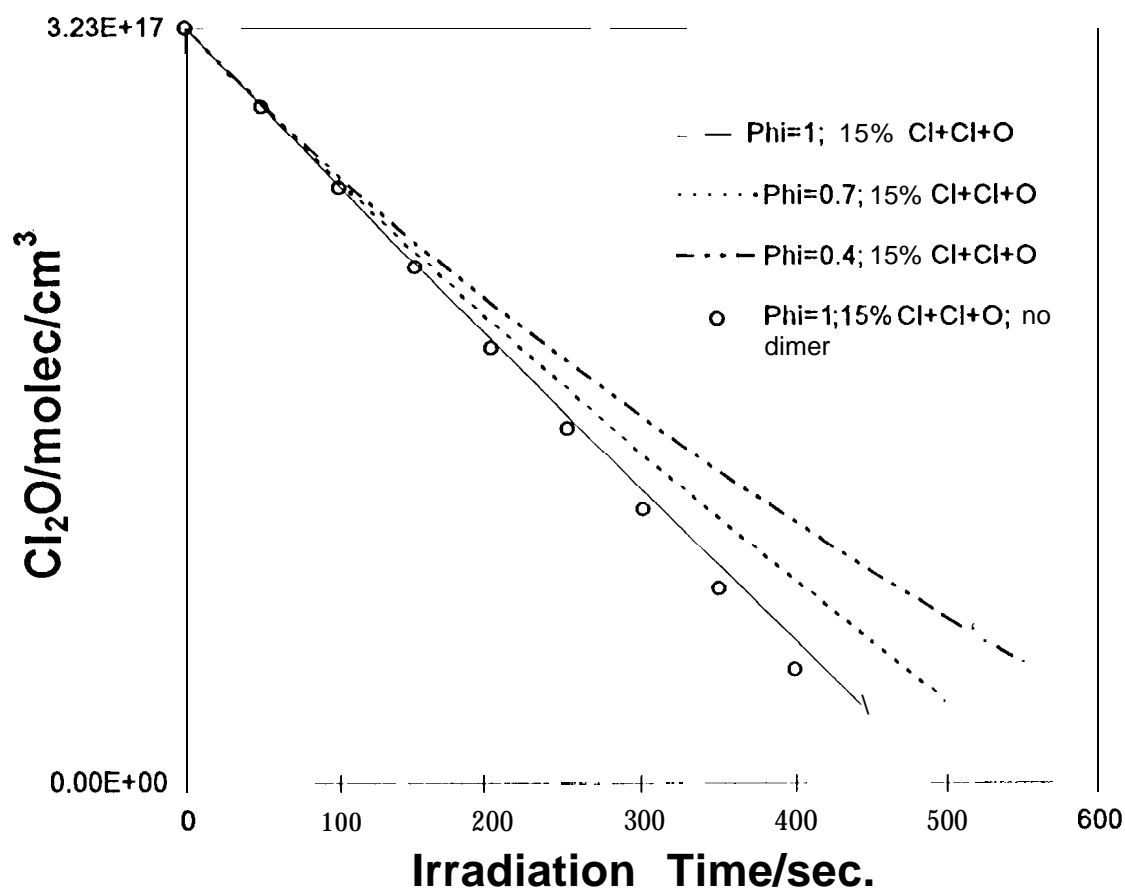


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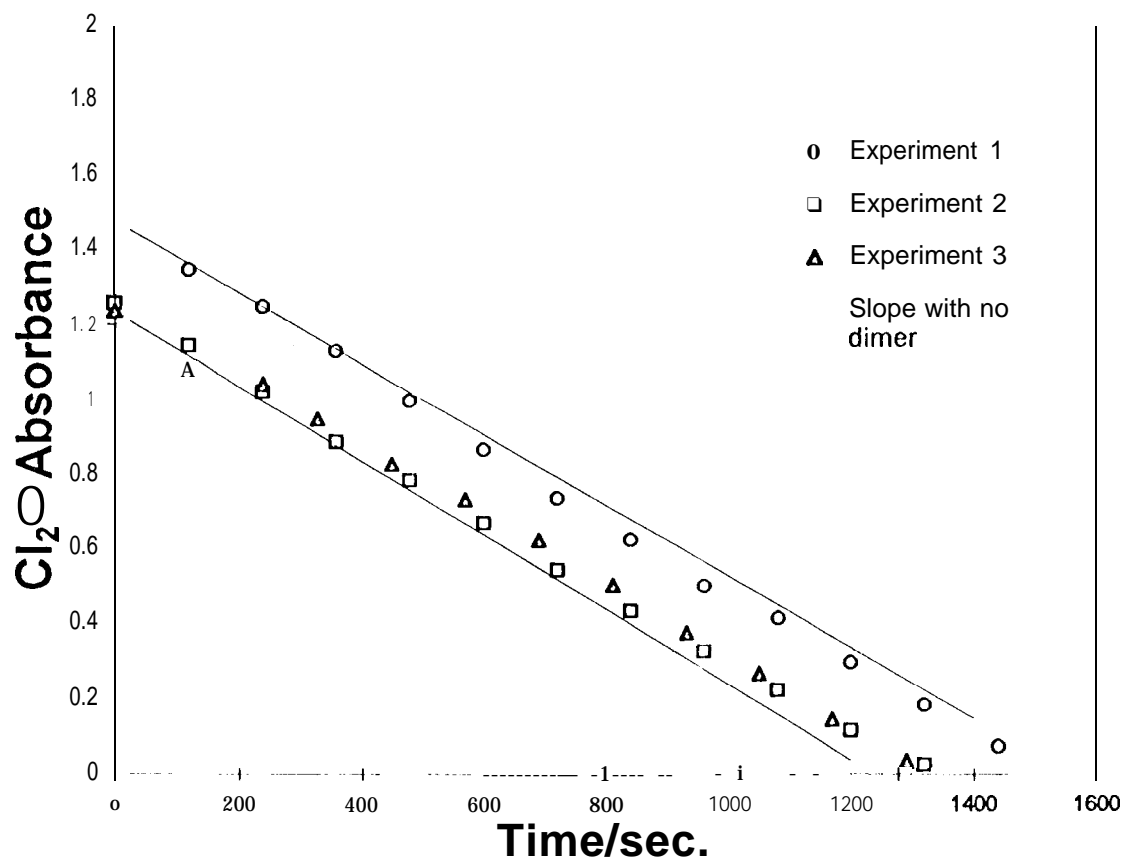


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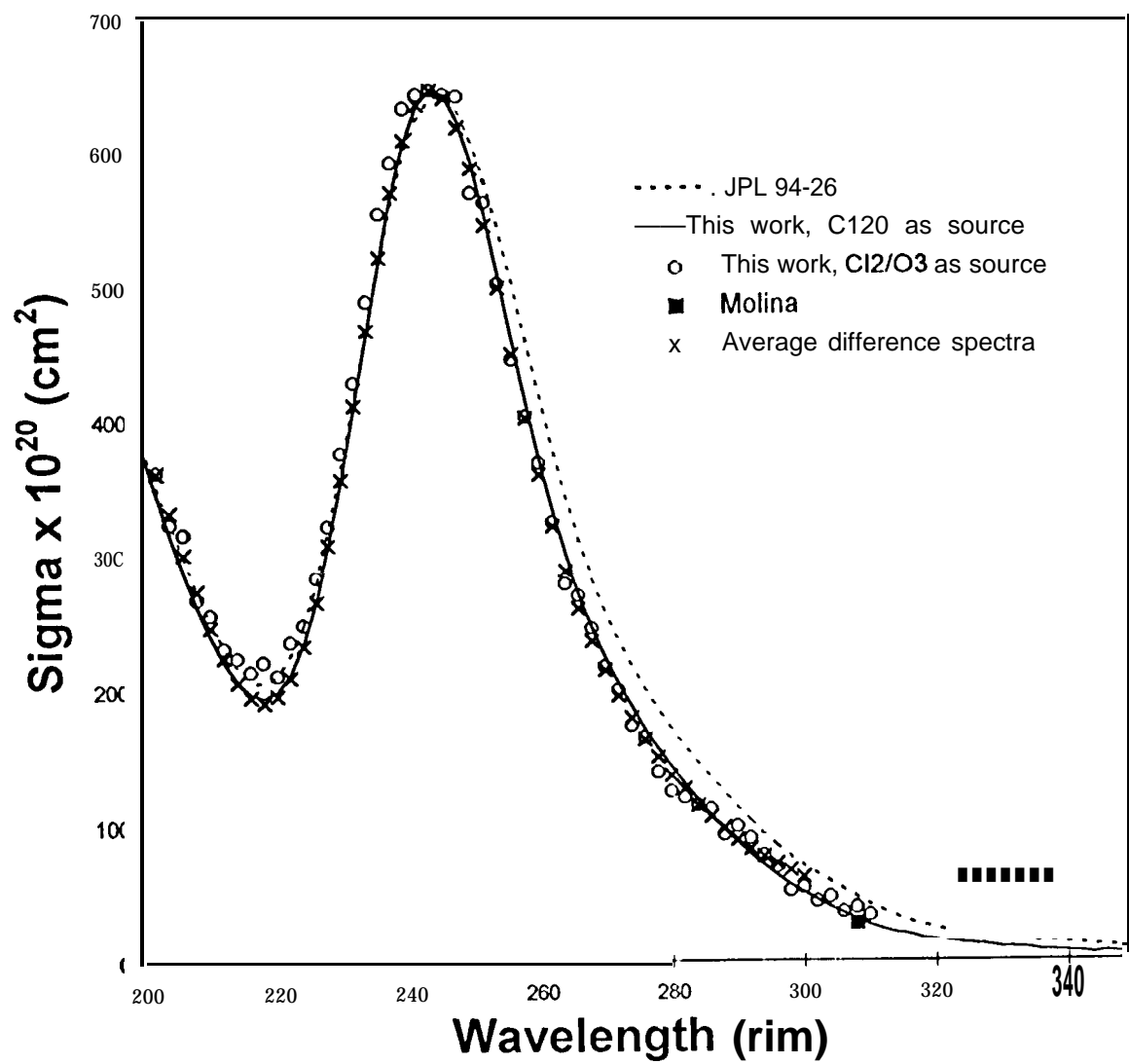


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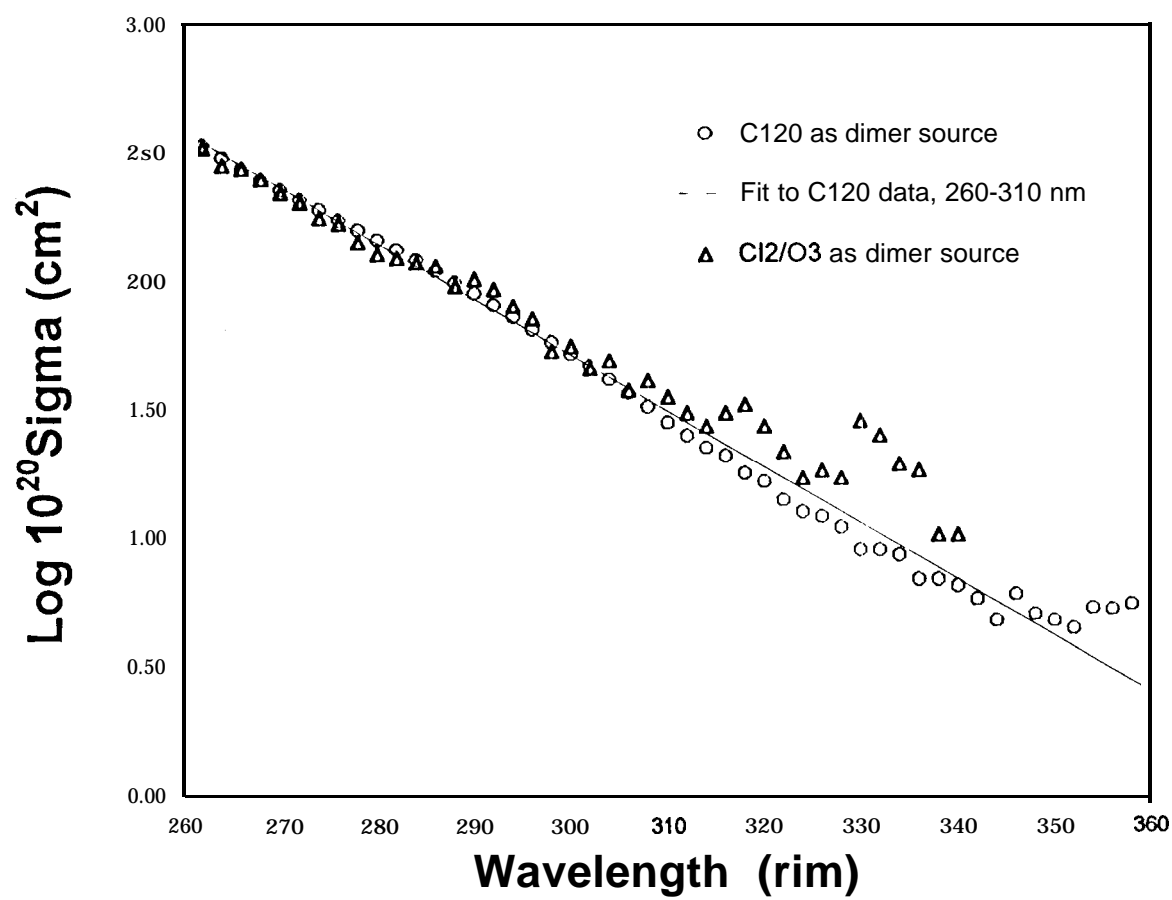


Figure 6: Huder and DeMore

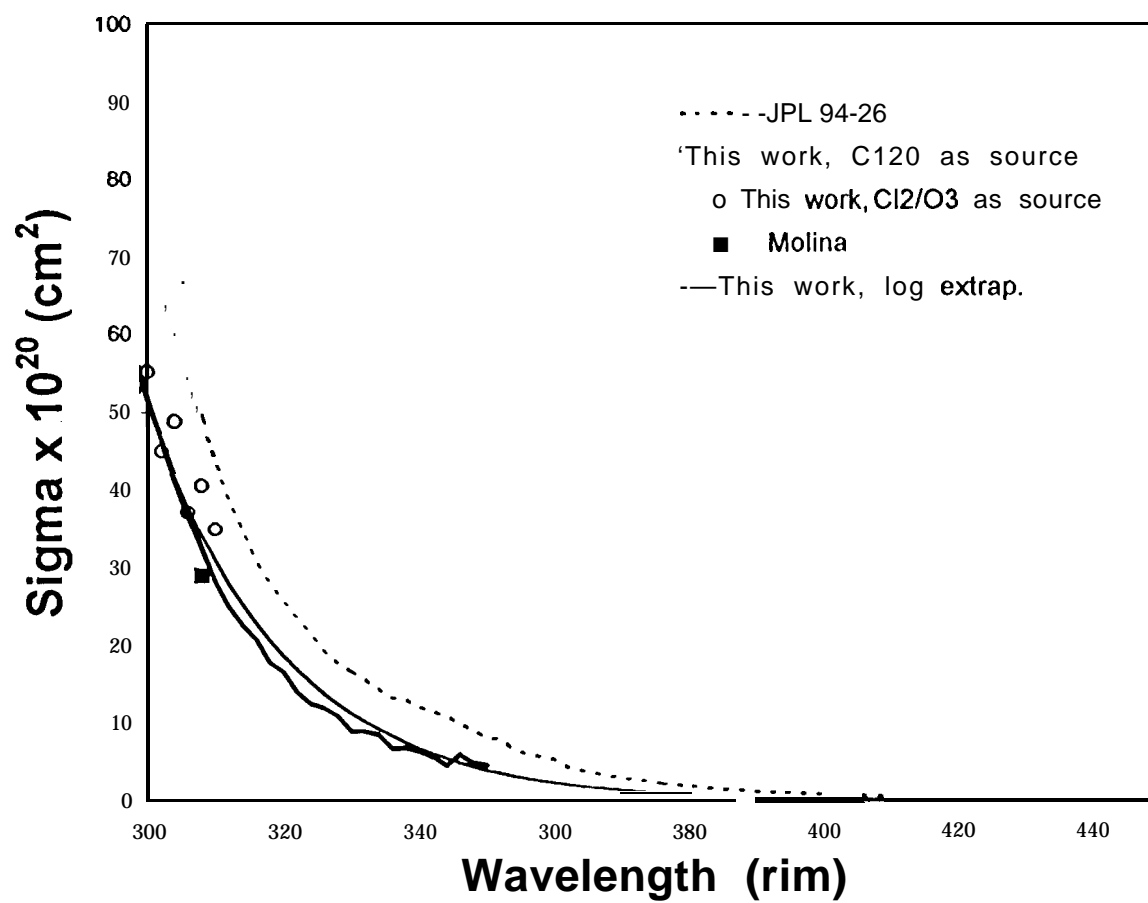
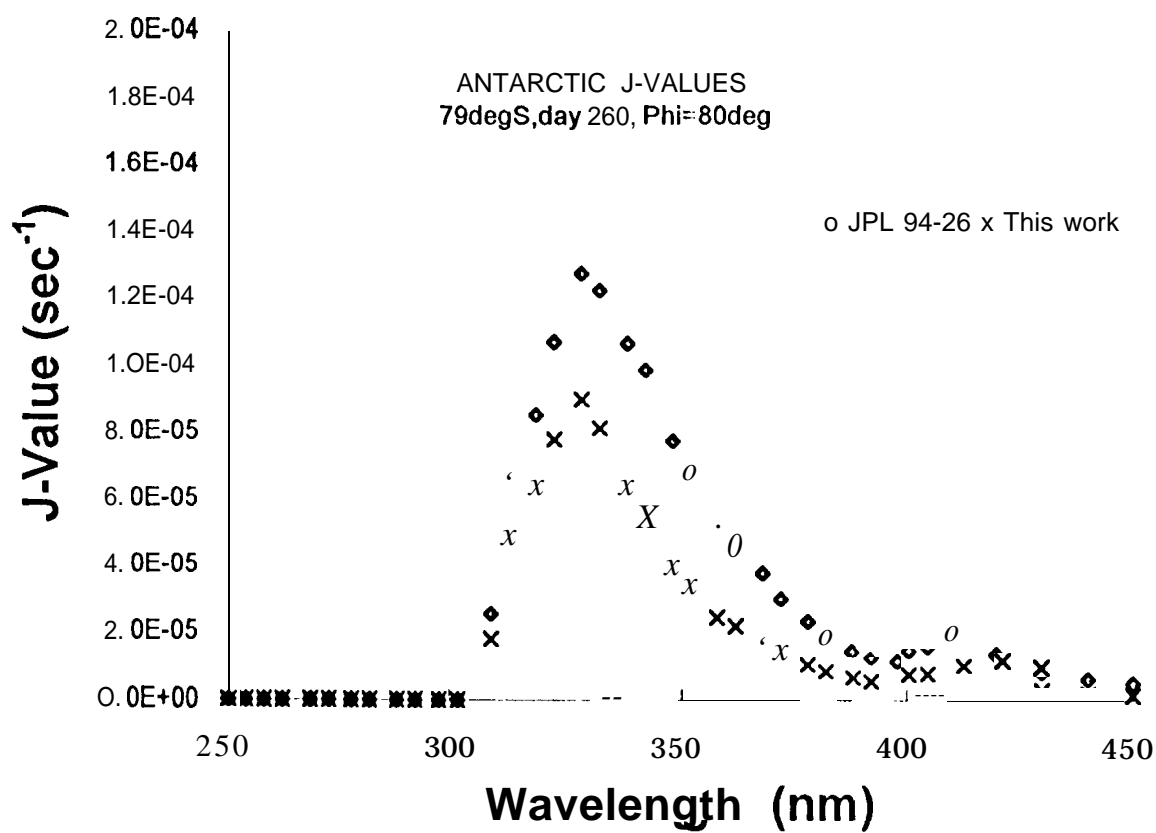


Figure 7: Huder and DeMore



Absorption Cross Sections of the ClO Dimer

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Abstract

The absorption cross sections of the ClO dimer, ClOOCi, are important to the photochemistry of the polar winter. In this work new measurements were made of the dimer cross sections. The results yield somewhat lower values in the long wavelength region, compared to those currently recommended in the NASA data evaluation (JPL 94-26). The corresponding Antarctic J-values are reduced by about 40%.

introduction

The ClO dimer is formed by the self-reaction of ClO radicals at the low temperatures of the earth's polar winter. When sunlight is present, the dimer is thought to take part in catalytic ozone destruction by yielding chlorine atoms upon photolysis, followed by attack of the chlorine atoms on ozone.



To model the role of ClOOCi in polar photochemistry, it is necessary to know its rate of formation, the photolytic cross sections, and the photolysis products. In addition to the path yielding Cl and ClOO radicals, another path yielding Cl() + ClO is possible.



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Since it is difficult to obtain reliable cross sections at longer wavelengths by direct experimental measurement (for reasons discussed above), we have concentrated on obtaining accurate data at shorter wavelengths. Those values can then be used for extrapolation above 310 nm. We have looked only at relative cross sections, since the absolute values near the peak are reasonably well established.³ The basic problem is to determine how much of the Cl_2O spectrum to subtract. Three approaches have been used: (1), From the product spectra for each experiment the individual spectra for each component were subtracted from the total spectrum, using the criterion that the peak in the resultant dimer spectrum should be fixed at 244 nm, as determined in earlier work.⁶ (2), Dimer spectra were obtained by taking advantage of the fact that its rate of decomposition in the cell (by wall reactions) is much faster than that of the other components (Cl_2O and Cl_2), and thus the dimer spectrum on a relative basis can be obtained by taking difference spectra. The dimer spectrum obtained by the difference method may be slightly contaminated with the Cl_2O spectrum, to the extent that decomposition of that species occurs during the time of the dimer decomposition. However, that dimer spectrum should correspond to an upper limit for Cl_2O content, and thus serve as a useful boundary condition for comparison with spectra obtained by the iterative subtraction method. (3), Difference spectra taken in the course of our earlier work,⁶ using Cl_2/O_3 mixtures as the dimer source, were compared with the present spectra. The earlier spectra, although less suitable for the measurement of absolute cross sections because of the much lower dimer concentrations, are nevertheless useful for comparison of the shape of the dimer spectrum obtained from the Cl_2O experiments.

Results

Figure 1 shows dimer spectra as obtained by methods (1-3) above, All have been normalized to $6.4 \times 10^{-18} \text{ cm}^2$ at 244 nm, this being the JPL 94-26² recommendation at that wavelength. The NASA recommendation is included for comparison, as is the single measurement at 308 nm by the Molina group (calculated from their ratio $\sigma^{245}/\sigma^{308} = 22$)². Our data are in good agreement among themselves and with the Molina measurement, but are significantly lower than the JPL 94-26 recommendation in the tail, or fall-off region.

Figure 2 is a plot of the logarithms of the cross sections vs. wavelength, Also shown is a linear fit to the Cl_2O data based on the wavelength range 260-310 nm. Above about 310 nm, the logarithmic extrapolation is considered to be a better estimate of the cross sections than the actual data. The extrapolated data are compared in Figure 3 with the data and with JPL 94-26

recommendation. The latter is based on an extrapolation (above 360) nm of previous data ^{1,5,6}. **Table 1** lists recommended cross sections based on the present work.

Discussion

The present results strongly suggest that previous measurements of the dimer cross sections, on which the recommendations in JPL 94-26 (also 92-20) are based, were improperly corrected for Cl_2O , and are too high in the “tail” region. The current results also agree well with the 308 nm cross section value of the **Molina** group ². The **difference** has a significant effect on dimer **photolysis** rates in the Antarctic atmosphere. Most of the contributions to the **photolysis** rate occur at wavelengths in the 310 to 370 nm range. (See **Figure 4**). With the new cross sections the total J-value under Antarctic conditions is about 60% of that obtained from the JPL 94-26 cross sections.

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Table 1. Dimer Cross Sections, $\sigma, \text{cm}^2 \times 10^{20}$.

λ, nm	σ	λ, nm	σ	λ, nm	σ
200	374.6	284	119.4	368	1.7
202	342.8	286	107.9	370	1.5
204	312.8	288	97.2	372	1.4
206	285.3	290	88.5	374	1.2
208	260.5	292	79.5	376	1.1
210	238.3	294	71.5	378	1.0
212	219.9	296	63.7	380	0.92
214	205.9	298	56.9	382	0.83
216	196.7	300	51.3	384	0.75
218	193.7	302	46.0	386	0.68
220	198.3	304	41.6	388	0.62
222	211.5	306	37.7	390	0.56
224	233.2	308	34.1	392	0.50
226	264.8	310	30.8	394	0.46
228	304.7	312	27.9	396	0.41
230	352.8	314	25.2	398	0.37
232	406.6	316	22.8	400	0.34
234	461.6	318	20.6	402	0.30
236	515.2	320	18.7	404	0.28
238	563.6	322	16.9	406	0.25
240	602.4	324	15.3	408	0.23
242	628.7	326	13.8	410	0.20
244	640.0	328	12.5	412	0.18
246	637.1	330	11.3	414	0.17
248	619.1	332	10.2	416	0.15
250	588.9	334	9.2	418	0.14
252	549.5	336	8.4	420	0.12
254	505.1	338	7.6	422	0.11
256	458.1	340	6.8	424	0.10
258	413.0	342	6.2	426	0.09
260	370.1	344	5.6	428	0.08
262	332.1	346	5.1	430	0.07
264	299.0	348	4.6	432	0.07
266	269.7	350	4.1	434	0.06
268	245.2	352	3.7	436	0.06
270	223.3	354	3.4	438	0.05
272	204.2	356	3.1	440	0.05
274	187.6	358	2.8	442	0.04
276	170.9	360	2.5	444	0.04
278	157.1	362	2.3	446	0.03
280	143.3	364	2.1	448	0.03
282	131.0	366	1.9	450	0.03

Figure Captions

Figure 1. ClOOCl cross sections from this work compared to those of JPL 94-26.

Figure 2. Logarithmic plot of the cross section data.

Figure 3. ClOOCl cross sections at longer wavelengths.

Figure 4. Antarctic J-values for ClOOCl.

Figure 1: Huder and DeMore

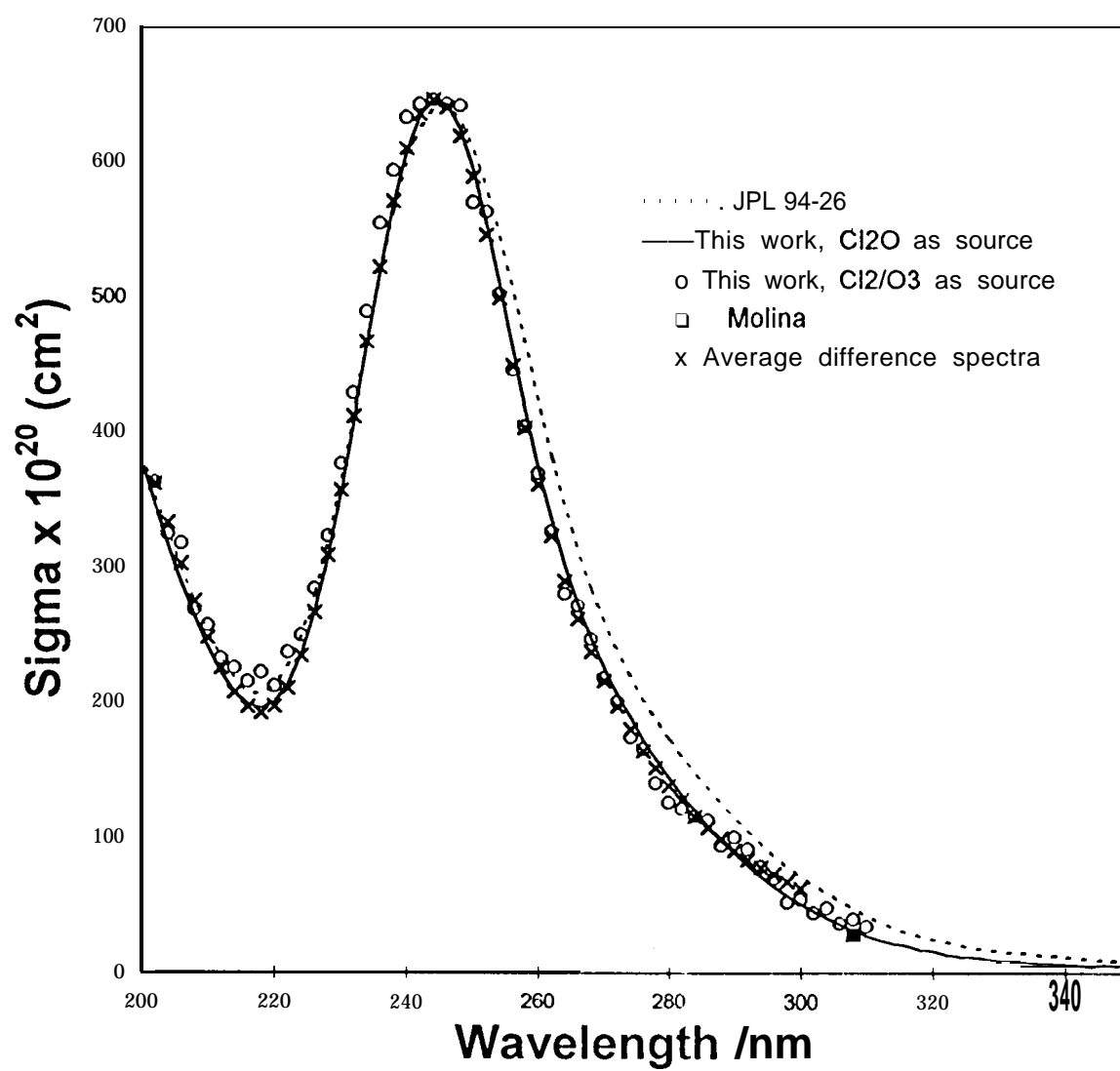


Figure 2: Huder and DeMore

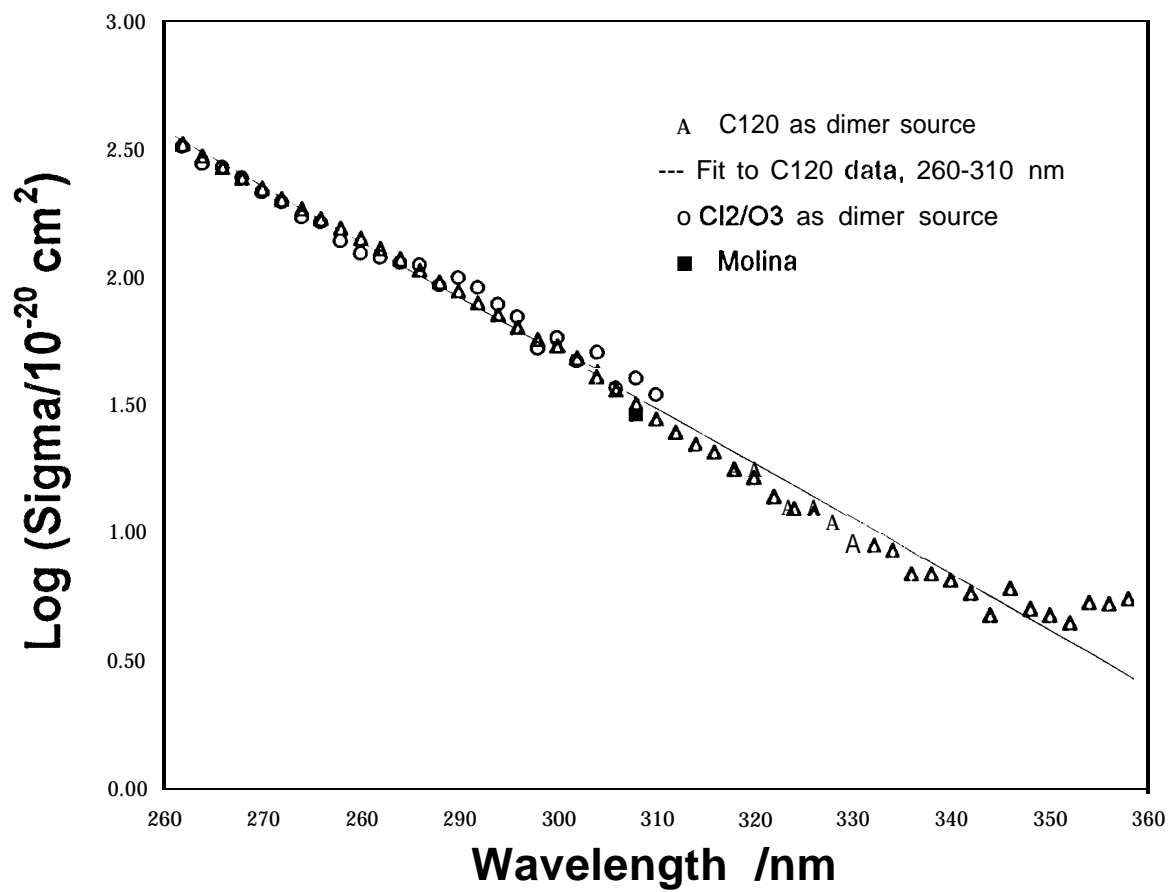


Figure 3: Huder and DeMore

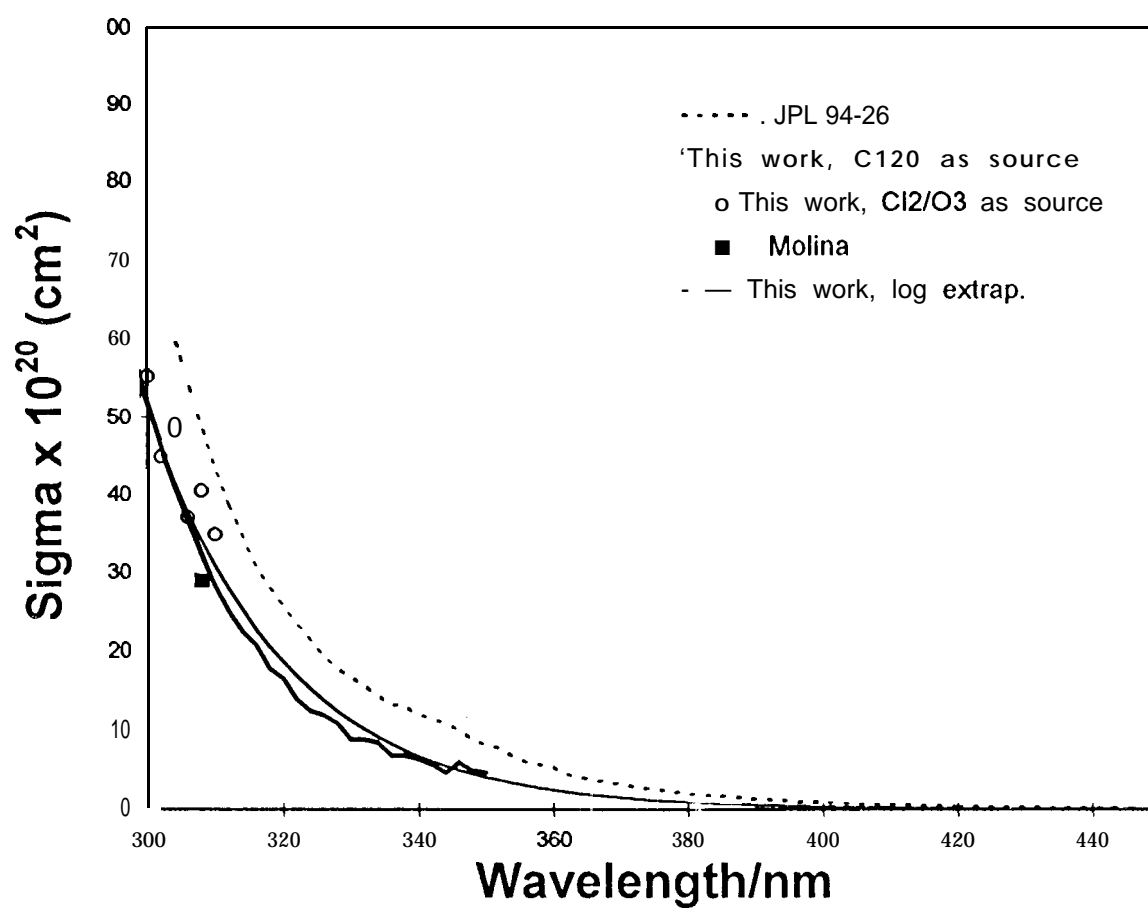


Figure 4: Huder and DeMore

